APPLICATION OF OLIVINE-SPINEL EQUILIBRIA TO EXTRATERRESTRIAL IGNEOUS SYSTEMS.

T.C. Prissel[1], J. Gross[1,2,3], and D.S. Draper[4]. [1]Department of Earth & Planetary Sciences, Rutgers University, Piscataway, NJ 08854. [2]American Museum of Natural History, New York, NY 10024. [3]Lunar & Planetary Institute, Houston, TX 77058. [4]Astromaterials Research Office, NASA Johnson Space Center, Houston, TX 77058. (contact: tcprissel@gmail.com).

Premise: This research is motivated by the recent development of a geothermometer based on aluminum partitioning within olivine-spinel co-saturated magmatic systems [1-2]:

$$T(^{o}C) = \frac{10{,}000}{0.512 + 0.873Y_{Cr} - 0.91\ln(K_D)} - 273$$

where Y_{Cr} = atomic proportion of Cr/(Cr+Al) in spinel and $K_D = Al_2O_3^{Ol}/Al_2O_3^{Sp}$ in wt.%. The Al-in-olivine geothermometer is calibrated at 1 bar, 1250 – 1450°C, FMQ + 1.3 to FMQ – 1.5, and predicts experimental temperatures within ± 20°C. Furthermore, experiments conducted at IW – 1 from [3] and 1GPa data from [4] do not display systematic deviation from the current calibrations (Fig. 1), indicating the Al-in-olivine geothermometer is applicable to planetary redox states and interior pressures. In similar fashion to many terrestrial ultramafic rock types (e.g., large igneous provinces, peridotites, primitive basalts), olivine and spinel ($[Mg,Fe][Al,Cr]_2O_4$) coexist in several extraterrestrial samples including: pallasites (interpreted to be samples from the core-mantle boundary of differentiated asteroids), martian olivine-phyric shergottites, and primitive lunar dunites and troctolites. Thus, the ubiquity of olivine-spinel-bearing igneous lithologies indicates the Al-in-olivine geothermometer can be broadly applied to constrain early thermal evolution of igneous provinces and differentiated bodies throughout the solar system.

In this abstract, we summarize the general application of olivine-spinel equilibria and Al-in-olivine geothermometry to extraterrestrial igneous systems and present preliminary Al-in-olivine data of main group pallasite Brahin 4859-1 as a case study.

Al-in-Olivine Geothermometry & Olivine-Spinel Equilibria: Perhaps the most common basis for determining the early thermal history of igneous samples relies on the temperature dependent partitioning of Mg between olivine and melt since olivine is the primary crystallizing silicate phase of most mantle-derived melts at low pressure [e.g., 5-8]. Olivine-melt geothermometry therefore has the advantage of estimating the crystallization temperatures of olivine-bearing samples, which in turn can be used to infer mantle potential temperatures of the terrestrial planets and Moon [8].

However, olivine-melt geothermometry can yield conflicting temperatures depending on estimates and assumptions of melt fraction, pressure of crystallization, and choice of the olivine-melt Fe-Mg equilibrium exchange coefficient, or $K_D^{Fe\text{-}Mg} = [X_{Fe}/X_{Mg}]^{ol} \times [X_{Mg}/X_{Fe}]^{liq}$ [e.g., 2,7,9-11]. For instance, olivine-melt geothermometry has been used both to argue for [10,11] and against [7,9] similar mantle potential temperatures below regions of intraplate volcanism and mid ocean ridges. Moreover, many natural olivine-bearing samples contain trace amounts of spinel, complicating estimates of liquidus temperatures obtained via olivine-melt equilibria alone [e.g., 1,2,12].

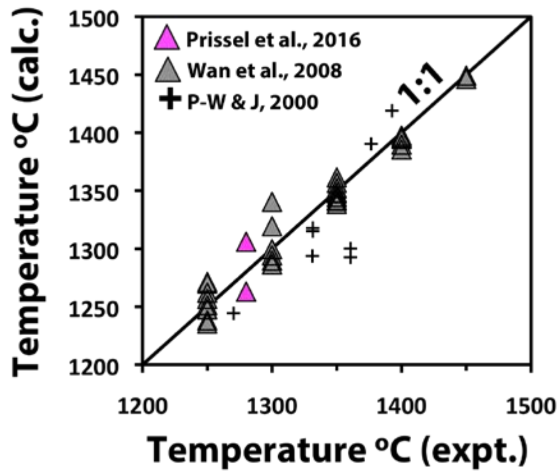

Fig. 1. Calculated and experimental temperatures using the Al-in-olivine geothermometer of [1] (grey-filled triangles, IW + 2.5), compared to 1-atm experiments from [3] (pink-filled triangles, IW - 1), and 1GPa experiments from [4] (plus-symbols, P-W & J). A 1:1 line is shown for reference (diagonal solid black line). The correlation of experimental data suggests the Al-in-olivine geothermometer is robust over a wide range of P-T-fO_2 extraterrestrial conditions.

Spinel is commonly interpreted to be a near-liquidus phase in natural rocks (supported by several experimental studies), occurring as euhedral to anhedral phenocrysts and crystalline inclusions within host-olivine [e.g.,1-3,12-14]. Therefore, olivine-spinel geothermometry estimates a near-liquidus co-saturation temperature (commonly within ~10°C of the liquidus) [2], providing minimum constraints on the liquidus temperatures of mantle derived melts. Similar to olivine-melt equilibria however, early olivine-spinel geothermometers relied on the temperature dependent partitioning of Fe-Mg, and could easily be reset during sub-solidus re-equilibration due to the rapid inter-diffusion of Fe-Mg between olivine and spinel [1,15]. Al-in-olivine geothermometry is less susceptible to short-lived changes in temperature and sub-solidus re-equilibration because the diffusion rates of Al are << Fe-Mg [1,2].

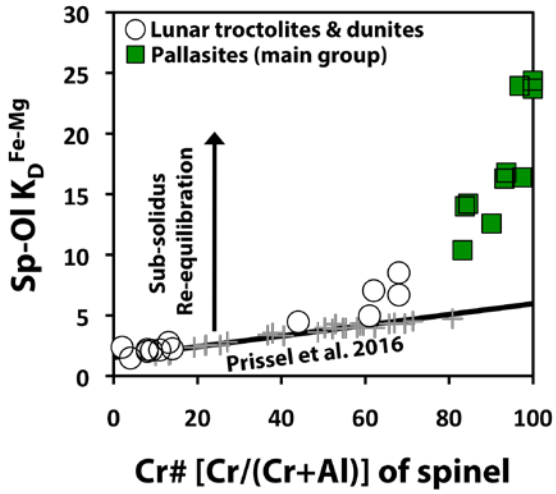

Fig. 2. Sp-Ol K_D^{Fe-Mg} = $[X_{Fe}/X_{Mg}]^{Sp}$ x $[X_{Mg}/X_{Fe}]^{Ol}$ correlated with the Cr# of spinel. The equilibrium line from [3] is shown for reference (solid near-horizontal black line). Symbol legend provided and equilibrium experimental data (grey plus symbols) from [1,3,16,17]. Due to the slow diffusion rates of Al relative to Mg-Fe, the Cr# of spinel is not expected to significantly change during sub-solidus re-equilibration. However, sub-solidus re-equilibration will increase the apparent Sp-Ol K_D^{Fe-Mg} to greater than equilibrium values as spinel incorporates Fe from olivine. Pallasites appear to have experienced significant sub-solidus re-equilibration relative to the lunar dunites and troctolites (shallow-level plutonic origin), consistent with their uniquely slow cooling histories (<10ºC/Ma). Natural data reported in [3(and references therein),18-20].

Although an accessory mineral in most igneous rocks, the presence and composition of spinel can constrain formation conditions and parental melt compositions of both terrestrial and planetary samples [12,13,15,21]. More recently, [3] demonstrated how olivine-spinel equilibria can also be used to both identify and correct for Fe-Mg sub-solidus re-equilibration in planetary samples (Fig. 2).

Brahin 4859-1: Pallasites are some of the slowest cooled samples (< 10ºC/Ma) among the planetary sample collection [22,23] and thus, Fe-Mg geothermometry has likely been reset during sub-solidus re-equilibration. Therefore, the Al-in-olivine geothermometer may provide an opportunity to place the most direct and robust thermal constraints of a planetary core-mantle boundary.

In the thick section studied here (Brahin 4859-1), the mantle component is primarily comprised of several euhedral olivine grains (~10's of mm in diam.; Fo# ~89) and two rounded euhedral to subhedral chromite grains (~5 mm in diam.; Mg# ~33; Cr# ~97). Utilizing the olivine-spinel equilibria methods of [3], Brahin 4859-1 and published data [17,18] from other chromite-bearing pallasites appear to have experienced significant sub-solidus re-equilibration relative to lunar dunites and troctolites (Fig. 2). Additionally, the uniquely slow cooling history of pallasites may have resulted in a near-complete equilibration of Al-abundance in both olivine and chromite.

Al-in-olivine concentrations collected via EPMA (Rutgers University, 15kv, 200nA and a focused beam) range from 0.001 – 0.005 wt.% throughout, with ~ 1.28 +/- 0.08 wt.% Al_2O_3 in chromite. Thus, Al-in-olivine geothermometry yields olivine-chromite co-saturation temperature estimates of ~1000 – 1290ºC, respectively. Al-in-olivine concentrations will be collected via LA-ICPMS (Rutgers University) where applicable in order to improve data resolution and also to test for and ensure reproducibility.

Summary: In general, Al-in-olivine geothermometry provides a necessary means to scrutinize planetary studies based on olivine-melt equilibria alone [1,2].

-- Al-in-olivine geothermometry may provide the unique opportunity to asses the formation temperatures of primary mantle cumulates (e.g., investigation of the main group pallasites).

-- Olivine-spinel equilibria can also be used to identify and correct for sub-solidus re-equilibration in planetary igneous rocks [3] (Fig. 2).

-- Further analysis of mantle-derived olivine-spinel-bearing extraterrestrial samples, including testing for Al-zoning within more rapidly cooled systems such as the shallow-level lunar plutonic troctolites and basaltic martian shergottites, can provide a better understanding of mantle potential temperatures during cumulate upwelling within the rocky planets and Moon.

Acknowledgments: We thank the American Museum of Natural History for the pallasite samples examined in this study.

References: [1] Wan, Z. et al. 2008 Am. Min. 93, 1142-1147 [2] Coogan, L.A. et al. 2014 Chem. Geol. 368, 1-10 [3] Prissel, T.C. et al. 2016 Am. Min. 101, 1624-1635 [4] Pickering-Witter, J. & Johnston, A.D. 2000 Cont. Min. Pet. 140, 190-211 [5] Roeder, P.L. & Emslie, R.F. 1970 Cont. Min. Pet. 29, 275-289 [6] Hess P.C. 1994 JGR 99, 19083-19093 [7] Herzberg, C. & O'Hara, M.J. 2002 J. Pet. 43, 1857-1883 [8] Putirka, K.D. 2016 Am. Min. 101, 819-840 [9] Putirka, K.D. et al. 2007 Chem. Geol. 241, 177-206 [10] Green, D.H. et al. 2001 Eur. J. Min. 13, 437-451 [11] Falloon, T.F. et al. 2007 Chem. Geol. 241, 207-233 [12] Kamenetsky, V.S. et al. 2001 J. Pet. 42, 655-671 [13] Prissel, T.C. et al. 2014 EPSL 403, 144-156 [14] First, E. & Hammer, J. 2016 MAPS DOI:10.111/maps.12659 [15] Irvine, T.N. 1965 Can. J. Earth. Sci. 2, 648-672 [16] Elkins-Tanton, L.T. et al. 2002 EPSL 196, 239-249 [17] Green, D.H. et al. 1971 2nd LSC 1, 601-615 [18] Greshake, A. et al. 2003 GCA 68, 2359-2377 [19] Boesenberg, J.S. et al. 2012 GCA 89, 134-158 [20] Gross J. et al. 2013 MAPS 48, 854-871 [21] Gross, J. & Treiman, A.H. 2011 JGR 116, E10009 [22] Buseck, P.R. & Goldstein, J.I. 1969 Bull. Geol. Soc. Am. 80, 2141-2158 [23] Yang, J. et al. 2010 GCA 74, 4493-4506